

## The Effect of Support

To investigate the effect of support on performance, ZrO<sub>2</sub> and TiO<sub>2</sub> supported catalysts were studied. From FIG. 5a it is seen that the activity of the Al<sub>2</sub>O<sub>3</sub> far exceeds that of the other supports. The minimum CO level for the 3-ZrO<sub>2</sub> and 3-TiO<sub>2</sub> catalysts was 3080 ppm, and 636 ppm, respectively. Furthermore, the hydrogen consumption quickly accelerates for these catalysts once a minimum CO level is attained, as shown in FIG. 5b. This can be attributed to the fact that the surface areas are much less; 69 and 9 m<sup>2</sup>/g for the zirconia and titania supports, respectively (found in Table 1). Lower surface area catalysts yield more poorly dispersed catalysts. The Al<sub>2</sub>O<sub>3</sub> catalyst with a higher surface area of 233 m<sup>2</sup>/g, and better dispersion, enables CO methanation to occur quicker, at lower temperatures, and more selectively, before CO<sub>2</sub> methanation predominates at higher temperatures. The activity increases with surface area in the order of Al<sub>2</sub>O<sub>3</sub>>ZrO<sub>2</sub>>TiO<sub>2</sub>.

## Stability Under Oxidizing Conditions

One concern some have concerning fuel processing catalysis has to do with the catalyst stability under actual operating conditions. One potential problem could be catalyst exposure to air, possibility at reaction temperatures. FIG. 4 shows that catalyst is relatively active without any pretreatment, although the catalyst could be optimized with increasing reduction temperature. The durability of the catalyst was further tested by exposing the catalyst to air at reaction temperature (260° C.) for one hour, shutting down to room temperature under air, then starting up the next day after having left the catalyst flowing under air. From FIG. 6 it can be seen that the catalyst performance was not adversely affected. In fact, the catalyst selectivity was enhanced, as shown in FIG. 6b. After having run under operating conditions up to 300° C., the non-prereduced catalyst had selectivities comparable to the catalyst prereduced at 350° C., even after being exposed to air at reaction temperatures.

The performance of selective CO methanation catalysis is markedly affected by metal loading, pretreatment, and reduction parameters. Surprisingly, these conditions can be controlled to result in a highly active and selective CO methanation catalyst. It was shown that a high surface area support produces superior CO activity. The crystallite size may be controlled, and preferably increased, to suppress CO<sub>2</sub> methanation.

What is claimed:

1. A catalyst comprising:

Ru disposed on an alumina support;

wherein the Ru comprises at least about 1 weight % of the catalyst; and

wherein the catalyst is characterizable by a methanation selectivity, as measured by a test in which a gas mixture containing 0.9% CO, 24.5% CO<sub>2</sub>, 68.9% H<sub>2</sub>, and 5.7% H<sub>2</sub>O is exposed to the catalyst at a GHSV of 13,500 hr<sup>-1</sup> and a temperature of 240° C. wherein a product gas is produced,

such that 20% or less of the H<sub>2</sub> is consumed and the product gas comprises 100 ppm CO or less.

2. The catalyst of claim 1 comprising 3% to about 7% Ru.

3. The catalyst of claim 1 consisting essentially of Ru and alumina.

4. The catalyst of claim 3 wherein the Ru has an average particle size of 10 nm or greater as measured by XRD.

5. The catalyst of claim 1 wherein the Ru comprises at least about 3 weight % of the catalyst; and

having a surface area of at least 150 m<sup>2</sup>/g.

6. The catalyst of claim 5 wherein the catalyst is characterizable by a methanation selectivity, as measured by a test in which a gas mixture containing 0.9% CO, 24.5% CO<sub>2</sub>, 68.9% H<sub>2</sub>, and 5.7% H<sub>2</sub>O is exposed to the catalyst at a GHSV of 13,500 hr<sup>-1</sup> and a temperature of 240° C. wherein a product gas is produced,

such that 15% or less of the H<sub>2</sub> is consumed and the product gas comprises 30 ppm CO or less.

7. The catalyst of claim 6 consisting essentially of Ru and alumina.

8. The catalyst of claim 7 wherein the alumina consists essentially of gamma alumina.

9. The catalyst of claim 5 wherein the catalyst is characterizable by a methanation selectivity, as measured by a test in which a gas mixture containing 0.9% CO, 24.5% CO<sub>2</sub>, 68.9% H<sub>2</sub>, and 5.7% H<sub>2</sub>O is exposed to the catalyst at a GHSV of 13,500 hr<sup>-1</sup> and a temperature of 220° C. wherein a product gas is produced,

such that 5% or less of the H<sub>2</sub> is consumed and the product gas comprises 30 ppm CO or less.

10. The catalyst of claim 9 comprising 3% to about 7% Ru.

11. The catalyst of claim 10 wherein the Ru has an average particle size of 10 nm or greater as measured by XRD.

12. The catalyst of claim 5 wherein the Ru has an average particle size of 10 nm or greater as measured by XRD.

13. The catalyst of claim 1 wherein the catalyst is characterizable by a methanation selectivity, as measured by a test in which a gas mixture containing 0.9% CO, 24.5% CO<sub>2</sub>, 68.9% H<sub>2</sub>, and 5.7% H<sub>2</sub>O is exposed to the catalyst at a GHSV of 13,500 hr<sup>-1</sup> and a temperature of 240° C. wherein a product gas is produced,

such that 5% to 20% of the H<sub>2</sub> is consumed and the product gas comprises about 20 to 100 ppm CO.

14. The catalyst of claim 1 made by impregnating an alumina support with a Ru-containing solution in a single impregnation.

15. A catalyst comprising:

Ru disposed on an alumina support;

wherein the Ru comprises at least about 1 weight % of the catalyst; and

wherein the catalyst is characterizable by a methanation selectivity, as measured by a test in which a gas mixture containing 0.9% CO, 24.5% CO<sub>2</sub>, 68.9% H<sub>2</sub>, and 5.7% H<sub>2</sub>O is exposed to the catalyst at a GHSV of 13,500 hr<sup>-1</sup> and a temperature of 240° C. wherein a product gas is produced,

such that 20% or less of the H<sub>2</sub> is consumed and the product gas comprises 100 ppm CO or less; and

wherein the Ru has an average particle size of 10 nm or greater as measured by XRD.

16. The catalyst of claim 15 wherein the alumina comprises gamma alumina.

17. The catalyst of claim 15 comprising 3% to about 7% Ru.

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